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Crystallization in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass under pressure

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The effect of pressure on the crystallization behavior of the bulk metallic glass-forming $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy with a wide supercooled liquid region has been investigated by *in situ* high-pressure and high-temperature x-ray powder diffraction measurements using synchrotron radiation. In the pressure range from 0 to 3 GPa, the crystallization temperature increases with pressure having a slope of 19 K/GPa, which can be explained by the suppression of atomic mobility. This observation is opposite to the results of W.H. Wang, D.W. He, D.Q. Zhao, and Y.S. Yao [Appl. Phys. Lett. **75**, 2770 (1999)], reporting a decrease of the crystallization temperature under pressure in a pressure range of 0–6 GPa for the bulk glass $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ alloy. Compressibility with a volume reduction of approximately 22% at room temperature does not induce crystallization in the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk glass alloy. This indicates that the densification effect induced by pressure in the pressure range investigated plays a minor role in the crystallization behavior of this bulk glass alloy. The different crystallization behavior of the carbon-free and the carbon-containing glassy alloys has been critically assessed. © *2000 American Institute of Physics.* [S0003-6951(00)01448-0]

Recently, after the discovery of several families of multicomponent alloys exhibiting a large supercooled liquid region before crystallization such as La–Al–Ni, Zr–Al–Cu–Ni, and Zr–Ti–Cu–Ni–Be systems,[1–3] bulk metallic glass formation has become a common phenomenon. Since then there has been considerable interest in this field.[4] These materials possess an extremely high glass forming ability and high thermal stability against crystallization. For example, a cooling rate of only about 1 K/s is required to suppress crystallization and to form a metallic glass for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy, which is one of the most studied bulk metallic glasses.[5] The crystallization process of the alloy has been intensively investigated.[5–8] It was found that prior to crystallization, phase separation into two amorphous phases occurs, i.e., a Zr- and Ti-rich phase, and a Be-rich phase. A high nucleation rate is found in the decomposed regions. With further annealing, crystallization occurs. At low temperatures ($<\sim$750 K) the first primary crystals are a Be-rich phase with $MgZn_2$-type structure while a Zr_2Cu-like phase forms at higher temperatures. Long-range atomic diffusion is required for the crystallization in the alloy.[6,7] Hence, one might expect an increase of the crystallization temperature when an external pressure is applied, as it is observed in many conventional metallic glasses where long-range atomic diffusion processes are needed for crystallization. Recently, Wang and co-workers,[9] studied the effect of pressure on the crystallization temperature of a carbon-containing bulk glass $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ alloy and found that the higher the external pressure, the lower the crystallization temperature with a reduction rate of about 16 K/GPa. This result is somewhat surprising because long-range atomic diffusion processes are required for the crystallization for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. In this letter, we present *in situ* high-temperature and high-pressure x-ray powder diffraction investigations on the crystallization process of this alloy using synchrotron radiation. We found an enhancement of the crystallization temperature with pressure having a rate of 19 K/GPa. The different results for carbon-free and carbon-containing glassy alloys were critically assessed.

The bulk glass-forming $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy was prepared from high purity elements (Goodfellow, Zr from Teledyne with typically 99.995 purity and about 200 ppm oxygen). The master alloy was remelted in a Buehler melt-spinning device (modified for copper mold casting) and injection cast into the copper mold under high purity argon (99.9999%). The alloy rod prepared has a diameter of 3 mm and a length of 50 mm. For synchrotron radiation x-ray powder diffraction measurements, small pieces with a size around 0.5 mm were filed from the alloy rod. The amorphous structure of the filed particles was verified by x-ray powder diffraction. Thermal analysis was performed in a Perkin–Elmer DSC 7 differential scanning calorimeter at a heating rate of 40 K/min under a flow of purified argon. The alloy exhibits an endothermic event characteristic of the glass transition, followed by several characteristic exothermic events indicating a multistage crystallization process. It was found

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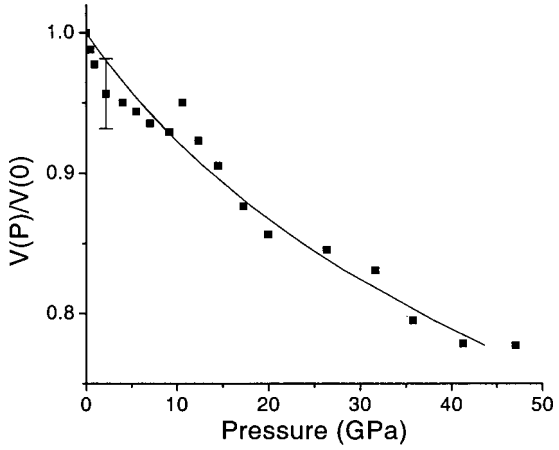

FIG. 1. Compression data of the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy at room temperature. Solid curve is calculated from the Birch equation of state.

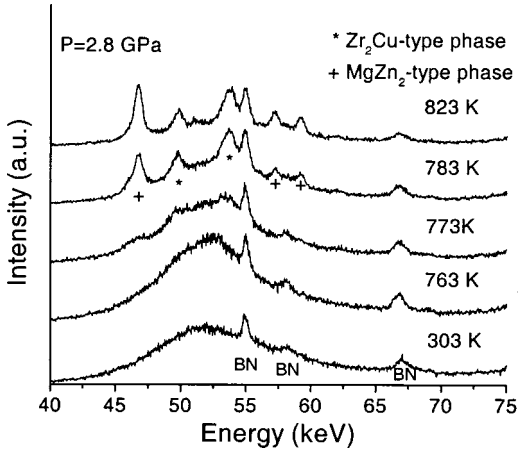

FIG. 2. Energy-dispersive x-ray powder diffraction patterns of the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy at 2.8 GPa and various temperatures. $Ed=119.224$ keVÅ.

that the glass transition temperature T_g, estimated as the onset temperature of the glass transition event, is 637 K, the onset temperature of crystallization $T_x=733$ K, and $\Delta T=T_x-T_g=96$ K. These data agree well with the data reported in the literature for this alloy, given the different heating rates of 10 or 20 K employed in these studies.[3,6]

In situ high-pressure and high-temperature energy-dispersive x-ray powder diffraction (EDXRPD) measurements were performed using synchrotron radiation at HASYLAB in Hamburg, Germany.[10] The temperature is measured by means of a thermcouple voltage with a stability of ± 1 K. The pressure of the sample is calculated from the lattice constant of NaCl using the Decker equation of state.[11] In addition, we have also carried out room-temperature compression EDXRPD measurements up to about 50 GPa using a diamond-anvil cell. A pressure transmitting medium of 4:1 methanol:ethanol solution was used. The actual pressure was calculated from the wavelength shift of the ruby line using the nonlinear pressure scale of Mao and co-workers.[12]

A large number of EDXRPD patterns of the bulk metallic glass were recorded at pressures ranging from 0~50 GPa at room temperature. Up to a pressure of approximately 50 GPa, no crystalline phase was observed. This fact suggests that thermal activation is necessary to induce crystallization in the pressure range used. The position of the main broad x-ray diffraction maximum was found to increase with pressure. In a dense random packed structure, the position (in $Å^{-1}$) is proportional to $1/d$, where d is the nearest neighbor distance in the bulk glass deduced from the position of the first peak in the radial distribution function curve (in Å).[13] This means that the corresponding nearest neighbor distance decreases with pressure. If one assumes that the density of the amorphous alloy is proportional to $1/d^3$ (Ref. 10), one can estimate the ratio of the volume at a given pressure to that at zero pressure, $V(p)/V(0)$, of the metallic glass. As shown in Fig. 1, the volume ratio decreases monotonically with pressure. At ~50 GPa, the glassy alloy has contracted by ~22%. The pressure-volume data shown in Fig. 1 were subsequently fitted to the Birch equation of state.[14] The zero-pressure bulk modulus is found to be 107 ± 10 GPa, which is in good agreement with the data for this alloy reported by other groups.[15]

In situ high-temperature EDXRPD measurements of the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy were performed in a pressure range of 0–3 GPa. The crystalline phases determined from the EDXRPD patterns recorded are identical in the pressure range used. Figure 2 exemplifies EDXRPD patterns recorded for the sample at 2.8 GPa and various temperatures. Up to 763 K, the amorphous structure is retained without clear indications for crystallization. At 773 K, very small and broadened crystalline peaks appear. The crystalline peaks become narrower in width and higher in intensity with increasing temperature and can be attributed to Zr_2Cu-type and $MgZn_2$-type phases.[7] Figure 3 shows the crystallization temperature, which was estimated from EDXRPD patterns recorded by increasing the temperature with a stepsize of about 10 K, as a function of pressure. It found that the applied pressure strongly affects the crystallization temperature of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk glass. The crystallization temperature increases with pressure having a rate of 19 K/GPa. A similar increase of the crystallization temperature under pressure in a range of 0–2.5 GPa was also observed for the $Fe_{72}P_{11}C_6Al_5B_4Ga_2$ metallic glass with a wide supercooled liquid region.[10]

Under pressure, densification of the material occurs, which reduces the free volume in the glass. This effect could favor the crystallization process because crystallization of metallic glasses involves the formation of crystalline phase(s) with higher density.[15] However, Fig. 1 reveals that no crystallization occurs at room temperature in the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy upon a volume reduc-

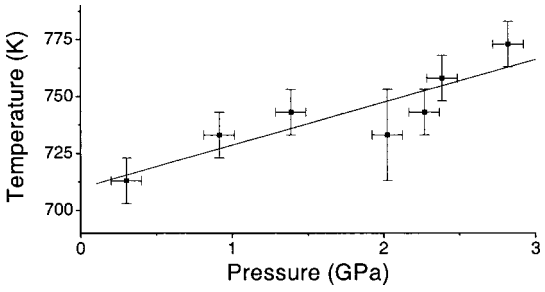

FIG. 3. Crystallization temperature of the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy as a function of pressure. The data were linearly fitted as a solid line.

tion of approximately 22% which is much larger than the free volumes (of usually a few percent) reported for metallic glasses.[16] In the metallic glass $Fe_{72}P_{11}C_6Al_5B_4Ga_2$ alloy with a wide supercooled liquid region, the amorphous state still remains in the sample for approximately 10% contraction in volume.[10] These results suggest that densification induced by external pressure does not have any important influence on the crystallization temperature of these metallic glasses with wide supercooled liquid region. Another pressure effect could be the reduction of atomic mobility, which results in retardation of the crystallization where long-range atomic diffusion is necessary for crystallization. A reduction of atomic diffusion constants with increasing pressure was reported in a similar ZrTiCuNiBe alloy.[17] This indicates a high thermal activation energy to be required for crystallization. It was mentioned that in the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy, prior to crystallization, phase separation occurs in which long-range atomic diffusion processes are already involved. With further annealing, intermetallic compounds nucleate in the phase separated regions. For this long-range atomic diffusion processes are most likely required too. Therefore, it is not unreasonable to expect a high temperature to be required for crystallization of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk glass, as observed in this study. Our observation of the pressure effect on crystallization temperature in the alloy is clearly different from that reported in Ref. 9. Some plausible explanations for this striking difference might be (1) different composition, 1 at % *C* in the sample used in Ref. 9 might lead to a different crystallization process in comparison to the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy; (2) the different techniques used to prepare samples; and (3) nonhydrostatic compression could accelerate the crystallization kinetics.[18] At ambient pressure, the carbon addition seems to retard crystallization compared to the carbon-free alloy, i.e., shifts the onset of crystallization to higher temperatures.[8] This was attributed to a more dense-packed structure of the supercooled liquid and a reduction in driving force for primary crystallization for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ alloy.[8] Moreover, carbon may form strong covalent bonds with the metallic constituents of the glass, which may also contribute to the suppression of crystallization at ambient pressure.[8] It should be noted that crystalline phases after crystallization for the carbon-containing and carbon-free glasses are different, although they have not been clearly identified in the carbon-containing glass.[9] It was stated (speculated) that a complex carbide may form in the carbon-containing glass[8,9] while only Zr_2Cu-type and $MgZn_2$-type phases are formed in the carbon-free glass observed in Fig. 2. Hence, it is suggested that the different pressure dependence of crystallization for the two different alloys may be related to the formation of a (metastable) complex carbide phase in the case of the alloy containing 1 at % C. High pressure perhaps induces a short-range rearrangement of atoms favoring formation of small clusters involving the carbon atoms, which may act as heterogeneous nucleation sites for crystallization. In addition, pressure may lower the activation energy for crystallization of a carbide phase and/or this phase could exhibit a change of free energy with pressure, which favors primary crystallization. This could explain why Wang and co-workers[9] found a reduction of the crystallization temperature for their alloy, while we observed an increase of T_x with increasing pressure.

In conclusion, the effect of pressure on the crystallization processes of the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy with a wide supercooled liquid region has been investigated by *in situ* high-pressure and high-temperature x-ray powder diffraction measurements using synchrotron radiation. It is found that the external pressure can strongly enhance the crystallization temperature of the metallic glass with a rate of 19 K/GPa. The behavior of crystallization temperature versus pressure is mainly governed by the suppression of atomic mobility under pressure. The densification effect induced by pressure in the range used does not have any important influence on the crystallization temperature of the bulk glass $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy. These results are opposite to the results of Wang and co-workers[9] reporting a decrease of the crystallization temperature under pressure in a pressure range of 0–6 GPa for the bulk glass $Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$ alloy. This discrepancy may be related to the 1 at % carbon in the sample used in Ref. 9 which might lead to a different crystallization process in comparison to the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy.

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